Study for Detection of Metallic Contaminant in Electrode of Lithium-ion Battery using a Hall Probe

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論 文 要 旨(修士)

論文題目	ホール素子を用いたリチウムイオン電池用電極中の金属異物の検出に関する研究

携帯電話やノートパソコン等のモバイル端末用電源に使用されているリチウムイオン電池は，その高エネルギー密度性故に，内部短絡等の不具合が発生した場合には発火・破裂に至ることもあり，その安全性が社会問題化している。電池製造工程における電池部材中への金属異物の混入は内部短絡を引き起こす一因となるため，電池の製造段階にて早期に検出する必要がある。現在，高温超電導SQUIDを用いた電池部材中の混入金属異物検出に関する検討が進められており，50μm程度の強磁性金属片を再現性良く検出できることが報告されているが，SQUIDの駆動に冷媒もしくは冷凍機が必要なため，装置が大型かつ高価になるという問題がある。一方，より小型・安価で汎用性の高い磁界センサの一つにホール素子がある。ホール素子の磁界検出感度はSQUIDよりも低いが，外部磁界を印加し電極中に混入した金属異物の発生磁界強度を増加させることで，金属異物の発生磁界を検出できる可能性がある。本研究では，ホール素子を用いてリチウムイオン電池用電極に混入した金属異物の磁界分布を測定し，より簡便かつ安価な金属異物検出技術としての適用可能性を検討することを目的とした。

Al箔上にコバルト酸リチウム（$LiCoO_2$）正極材料を塗布した電極（15mm×15mm，厚さ0.09mm）を作製し，この塗布電極に金属異物としてまず直径50μm，長さ0.5－2mmの鉄線を1個入れたものを試料とした。これをベークライト製の試料ホルダ上に固定し，試料面（x-y面）上で2次元的にホール素子を走査させながら，試料面に垂直な方向（z方向）の磁界分布測定を行った。測定に使用したホール素子（AREPOC製，型番HHP-VP）の感磁面積は50μm×50μmであり，素子の裏面にネオジム磁石を固定して，外部磁界（ホール素子表面で0.14Tおよび0.33T）を試料に印加した状態で測定を行った。測定間隔はx, y方向共に0.2mmとし，ホール素子と試料面との距離（リフトオフ距離）は0.5－3.5mmの範囲で変化させた。更に，鉄線での実験結果を踏まえた上で，60μmおよび80μm程度の平板状の鉄粉末を異物として塗布電極に混入させた場合についても測定を行った。

直径50μm，長さ1mmの鉄線を入れた$LiCoO_2$塗布電極面上の二次元磁界分布の測定結果では鉄線の磁化による磁界分布が観測できた。リフトオフ距離0.5 mmおよび2.5 mmのいずれの場合においても，鉄線位置の近傍において鉄線の磁化に伴う磁界変化を検出できることが確認できた。また，リフトオフ距離の増加と共に検出磁界強度は大きく低下するが，金属近傍の磁界ピークの形状はブロードになっており，より広い範囲で鉄線の磁化による磁界変化が現れることが確認された。鉄線（直径50μm）の長さを変化させた場合，検出磁界のピーク値 $B_{Z\text{-}max}$ は鉄線の長さにほぼ比例して増減することが確認され，粒径50μm程度の鉄粉末の有無を識別するためには，リフトオフを1mm以下にする必要があることが示唆された。また，測定感度向上に向けて，印加磁界（ホール素子表面）を0.14Tから0.33Tに増加したところ，鉄線からの検出磁界強度がほぼ倍増することを確認した。

以上の結果を踏まえて，60μmおよび80μm程度の平板状の鉄粉末を混入した塗布電極表面の磁界分布を印加磁界0.33T，リフトオフ0.5mmの条件で測定した。その結果，60μmの鉄粉末の場合，塗布電極自身が発生する磁界のため，鉄粉末の磁化による磁界変化は検出できなかったが，80μmの鉄粉末の場合，塗布電極の発生磁界に埋もれることなく鉄粉末の磁化による磁界変化を検出できた。今後，印加磁界方向とホール素子での検出磁界方向の組み合わせを調整することにより，更なる検出感度の向上を図ることが課題である。

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Abstract

Title	Study for detection of metallic contaminant in electrode of lithium-ion battery using a Hall probe.

Lithium-ion battery is commonly used for mobile power supply such as laptop and mobile telephone, because of its high energy density, but when malfunctions such as short circuit occurred inside battery, it could lead to ignition or explosion, and the battery safety is recognized as social problem. In process of battery production, metallic contaminant mix with parts of a battery can be a cause of short circuit inside battery. Therefore, it is necessary to detect at production stage. Study for detection metallic contaminant in battery using high temperature SQUID is currently in progress and by using this, 50μm ferromagnetic metal piece can be detected successfully. However, a cooling medium or cryogenic refrigerator is necessary for SQUID operation, so that the total measurement system becomes large size and expensive. On the other hand, Hall probe is known to be cheap and high versatility magnetic field sensor. Although measurement sensitivity of magnetic field for Hall probe is much lower than SQUID, by applying an external magnetic field can increase the field generated from magnetized metallic contaminant, resulting into increase for possibility to detect the metallic contaminant. In this research, we measured the magnetic field distribution of metallic contaminant in electrode for lithium-ion battery using Hall probe and examined the applicability for metallic contaminant detection technology that is more simple, easier and cheaper.

Electrode of lithium-ion battery (15mm×15mm, thickness 0.90mm) was made by coating cathode material, $LiCoO_2$ on Aluminum foil, and measurement sample were prepared by adding a piece of iron wire (diameter 50μm, length 0.5－2.0mm) on the electrode. The sample was put on a Bakelite sample holder, and a Hall-probe was placed on top of it and then was scanned two-dimensionally in x-y planar to examine distribution of magnetic field whose direction is perpendicular to sample surface (z-direction). Hall probe was made by AREPOC (HHP-VP) and its active area was 50μm×50μm. The field distribution of sample was measured under applied magnetic field by placing permanent neodymium magnet at the back of the probe. Applied external field that detected by probe were 0.14T and 0.33T. Measurement step for both x and y direction was 0.2mm, and probe lift-off distance from the sample surface was changed in 0.5－3.5mm. From the result of iron wire as a metallic contaminant, flat-shaped iron particle with diameter size of 60μm and 80μm was measured.

For electrode with iron wire with a diameter 50μm and a length 1mm, the field distribution of magnetized iron wire could be detected successfully. It was confirmed that the field from magnetized iron wire was detected at lift-off distance of both 0.5mm and 2.5mm. Also, when the lift-off distance was increased, detected field strength was decreased largely, while the peak width was appeared broad, and therefore, the field change caused by magnetized iron wire can be detected in wider range. In measurement for electrode with different length of iron wire but fixed diameter, maximum peak of detected field $B_{Z\text{-}max}$ was increased proportionally to the length. From this result, the lift-off distance to detect iron particle with 50μm diameter was suggested to be set to 1mm and smaller. In order to enhance the measurement sensitivity, when applied field was increased from 0.14T to 0.33T, detected field strength from the sample with iron wire was increased double. Based on these results, to measure electrode with flat-shaped iron particle with diameter of 60μm and 80μm, measurement condition of 0.33T of applied field and 0.5mm of lift-off distance was determined. For iron particle with diameter of 60μm, the field from iron particle could not be detected because the field from iron particle was disturbed by that from the electrode. For iron particle with diameter of 80μm, the field from iron particle was detected due to not buried by field from the electrode. The direction of applied field and detected field by Hall probe should be adjusted for further improvement of measurement sensitivity as a task to be considered in future.

Study for detection of metallic contaminant in electrode of lithium-ion battery using a Hall probe

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CHAPTER 1 Introduction

1.1 Research background and objective

Recently, contaminant mixed in the industrial goods such as foods and electronic equipment has become a big social issue. Contaminant have two types which are metallic contaminant such as small piece of zinc, nickel, stainless steel, and non-metallic contaminant like stone, glass, plastic. When metallic contaminant mixed in foods, the danger that will occur to the consumers are like mouth cut, broken teeth and other health damage (physically injury), and then these make the consumer having unpleasant impression and lead to feel repulsion to the goods. When metallic contaminant mixed in electronic parts and equipment, it will cause trouble such as defective operation, breakdown and ignition. For the manufacturer, the problems are the reliability of product decreased, large-scale recall of goods and etc. therefore, social need of the detection of contaminant in industrial goods at the early stage is very high.

In this laboratory, as the research for lithium ion battery, the metallic contaminant mixed in battery parts at the production stage becomes a serious problem from the viewpoint of safety. Lithium ion battery is widely used for mobile power supply such as laptop and mobile telephone, and currently expanding into larger power supply for electric vehicle, hybrid car, energy storage and etc. As in high energy density, when malfunctions such as short circuit occurred inside battery, it could lead to ignition or explosion, and the battery safety is recognized as social problem. In process of battery production, metallic contaminant mix with parts of a battery can be a cause of short circuit inside battery. Therefore, it is necessary to detect at production stage. Currently, there is a detection device by X-ray or X-ray inspection could detect metallic and non-metallic contaminant. But, metallic contaminant of diameter 100μm and less could not be detected. While, study for detection metallic contaminant in battery using high temperature Superconducting QUantum Interference Device (SQUID) is in progress and by using this, 50μm ferromagnetic metal piece could be detected successfully[1]. However, a cooling medium or cryogenic refrigerator is necessary for SQUID operation, so that the total measurement system becomes large size and expensive.

On the other hand, Hall probe is known to be cheap and high versatility magnetic field sensor. Although measurement sensitivity of magnetic field for Hall probe is much lower than SQUID, by applying an external magnetic field can increase the field generated from magnetized metallic contaminant, resulting into increase the possibility to detect the metallic contaminant.

In this research, we measured the magnetic field distribution of metallic contaminant in electrode for lithium-ion battery (coated electrode) using Hall probe and examined the applicability for metallic contaminant detection technology that is more simple, easier and cheaper.

1.2 Lithium-ion battery

1.2.1 Working principle of lithium-ion battery

Materials mainly used in lithium ion battery are lithium-containing transition metal oxide for positive electrode and graphitized-carbon material for negative electrode. The charge and discharge reaction of lithium ion battery is based on simple reaction of lithium ion move between the active material of positive and negative electrode through the electrolyte[2]. The working principle of lithium ion battery is, first of all, in the charge state of battery, lithium ion stored in positive electrode is detached and moved through the electrolyte and inserted between the interlayer of negative electrode (graphite electrode). By this movement of lithium ion and electron, lithium ion battery is charging. In the discharge state of battery, the movement of lithium ion and electron is reversed, which lithium ion stored in negative electrode is moved through the electrolyte and inserted into the positive electrode. Figure 1.1 illustrates the working principle of lithium ion battery (in the discharge state).

The best characteristic of lithium ion battery compared to Nickel-Metal Hydride (NiMH) battery, Nickel-Cadmium (NiCd) battery, lead acid battery and other secondary batteries or rechargeable batteries is high voltage, which about 4V. Therefore, water which has theoretical decomposition voltage 1.23V cannot be used as electrolyte, but non-aqueous electrolyte has to be used by dissolving electrolyte salt in organic solvent.

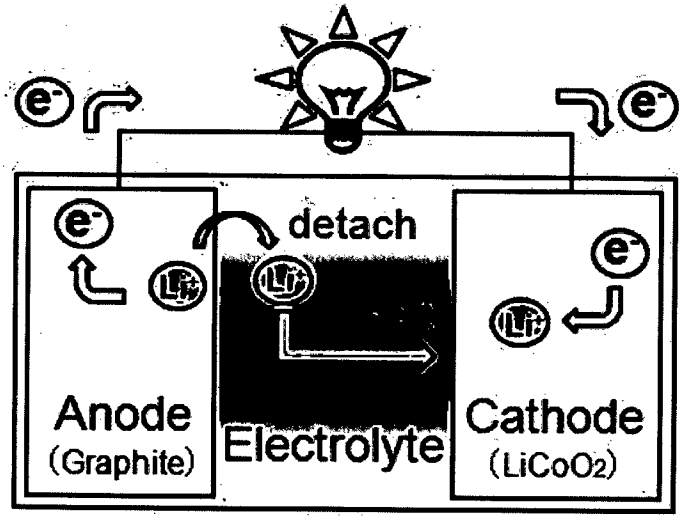

Figure 1.1 The working principle of lithium-ion battery (in the discharge state)

1.2.2 Characteristic of lithium-ion battery

Batteries have become useful in our general daily life and are put to even greater use of it in wider field in the future. Batteries are divided into two categories, primary batteries that have to disposal after used and secondary batteries that can be used again by charging. The later is in the charge state when electrical energy is applied and lead to chemical reaction. Thus, the secondary battery is a conversion and storage device of electrical energy into chemical energy. The secondary battery such as lithium ion battery, which is useful for mobile phone, laptop, car and etc., and as an efficient rechargeable battery, its existent is absolutely necessary for the society. Lithium ion battery, from the history of battery development, it has been used since 1991 and has characteristic such as small size, light weight, high open circuit voltage, and high energy density, etc. There are still continually having the demands for lithium ion battery even had been used about 20 years ago, and recently, not only in our daily life but also in other different kinds of field at sea, sky, space and many more is spread widely.

1.2.3 Application of lithium-ion battery

The production of Lithium ion battery was started by SONY in 1991[2]. At first, it was installed in video camera because of its merits which are small self-discharge and large energy density. After that, because of the introduction of battery for mobile phone (100% lithium ion battery currently installed) and laptop, its market has been expanded every year. At present, the application has expanded to electrical power tool, portable music device, game console and so on[4]. Especially lithium ion battery for car is being expected. In recent years, the influences of greenhouse effect caused by increasing exhausted carbon dioxide and sudden increased of oil and gas price had come to the surface globally, therefore in the industrial of car, hybrid vehicles, plug-in hybrid vehicles, and electric vehicles are being introduced to tackle these problems. In the present state, lithium ion battery for car has been started being sold and the demands will be expected to increase in the future.

1.2.4 Problem of lithium ion battery

The problem of lithium ion battery is there are market troubles of battery related to safety and battery recall since had been used in year 1995 until year 2007. Table 1.1 shows the recall of lithium ion battery.

From Table 1.1, the reason for recall of battery cases is more to internal short circuit[5]. Furthermore, other reason is exothermic phenomenon. When lithium ion battery is exposed to high temperature such as dropped into the fire, chemical reaction in lithium ion battery is rapidly occurred, these could resulted to start smokes, ignition, and explosion, and other hazardous situation. In addition, the contaminant mixed in during the production stage of battery or metal deposits inside battery can cause the internal short circuit and other occurred, as the reason of this, the temperature of battery is increased and the battery is chain reaction self-heated. In case of the heat dissipation is not enough, the smoke, the ignition, and other hazardous situation would be happened. The other reasons that generate self-heating of battery are thermal decomposition of electrolyte, reaction between cathode and electrolyte, and reaction between lithium insertion anode and electrolyte, etc.[5].

Table 1.1 The recall of lithium ion battery[5][6][7]

Year	Battery-used device	Trouble outline	Probable cause
1995	Note PC	Ignition	Abnormal charge
1996	Mobile phone	Explosion	Crush (internal short circuit)
1997	Note PC	Combustion	Internal short circuit (?)
1998	Note PC	Generation of heat	Short circuit by liquid leakage
1999	Note PC	Bag case melt	Internal short circuit (?)
1999	Video camera	Generation of heat	Short circuit by liquid leakage?
1999	Mobile Phone	Generation of heat and explosion	Internal short circuit
2000	Video Camera	Generation of heat and smoke	Short circuit by liquid leakage?
2000	Note PC	Ignition	Internal short circuit?
2000	Note PC	Generation of heat and smoke	Abnormal protection circuit?
2000	Mobile Phone	Swelled and could not be used	Poor weld?
2001	Mobile Phone	Generation of heat	Solder joint failure
2002	Mobile Phone	Ignition	Production failure?
2003	Mobile Phone	Generation of heat	Circuit fault?
2003	Mobile Phone	Explosion	Internal short circuit (non genuine product)

2004	PC	Ignition	Internal short circuit
2004	Fishing reel	Ignition	Internal short circuit
2005	Digital audio	Generation of heat	Internal short circuit
2005	Digital camera	Generation of heat	Internal short circuit
2005	DVD player	Generation of heat	Internal short circuit
2005	Mobile Phone (America)	Explosion	Internal short circuit?
2006	Mobile Phone	Battery pack swelled	Overcharged
2006	PC	Generation of heat and ignition	Internal short circuit
2006	PC	Generation of heat by fall	Battery pack production failure
2006	Scooter etc	Generation of heat and ignition	Internal short circuit
2006	Mobile Phone	Generation of heat and explosion	Internal short circuit
2007	PHS, Mobile Phone	Generation of heat by impact	Internal short circuit
2007	PC	Generation of heat and ignition	Internal short circuit
2007	Mobile Phone	Ignition and explosion	Internal short circuit
2008	Mobile Phone	Generation of smoke and ignition	Internal short circuit by external collision
2008	Digital audio	Ignition	Internal battery damaged by defective parts
2009	Note PC	Ignition and fire	Mixed with contaminant
2009	Portable TV	Generation of smoke and ignition	Under investigation
2011	Mobile Phone	Generation of heat	Internal short circuit

1.2.5 Probability of metallic contaminant mix in lithium ion battery at production stage

Figure 1.2 shows the standard production process of lithium ion battery. First of all, the slurry of electrode active materials mixture is made to make coating electrode (cathode and anode) of lithium ion battery. Then, electrode current collector is coated by the slurry using a coater, and winded up after dried. The thickness and width of the electrode is adjusted by roller press and cut using slitter. Here, there is a possibility that a small piece of iron and other metal from the slitter mix in the electrode. Furthermore, a group of electrode is put into battery tube after winded, then the terminal is put on and finally the battery is completed. There is a case that inside wall of the battery tube is coated by thin layer of nickel, and therefore there is a possibility that a small piece of nickel peel-off during swaging process and mix in the battery parts.

Metallic contaminant that mixes in lithium ion battery not only causing the battery longevity decreased, but also there is possibility to generate heat and the worst case is to cause the ignition. As its application for hybrid vehicle and electrical car would be introduced, the important to prevent metallic contaminant from mix into battery part is increased, and thus for this matter the prevention of metallic contaminant mix in during the production process of lithium ion battery is essential. In addition, the detection of metallic contaminant mix in the material, and the development of technology to detect at the early stage of production process are also important.

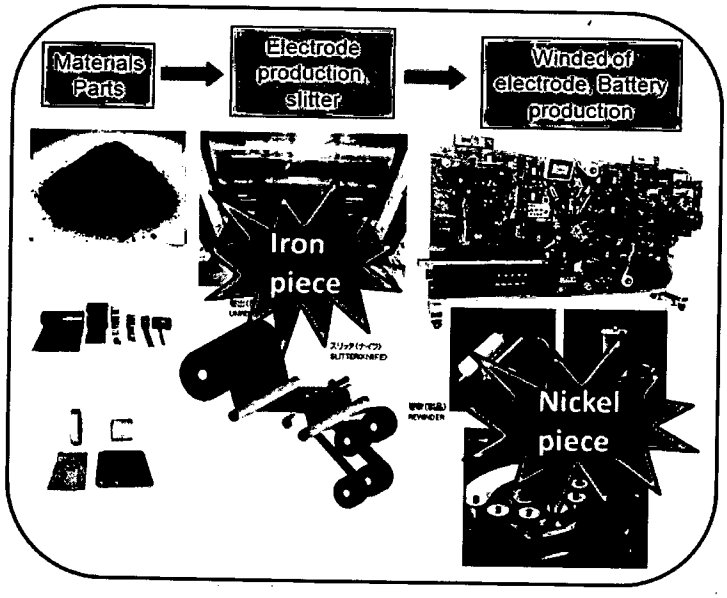

Figure 1.2 The possibility of metallic contaminant mix in during production stage of Lithium-ion battery

1.3 Metallic contaminant detection technology

1.3.1 X-ray inspection device

X-ray inspection device is configured with X-ray radiation tube that can generate soft X-ray, line sensor that can measure X-ray transmission amount and etc. X-ray that generated from radiation tube is transmitted through inspection goods and then the transmission rate is measured by line sensor. When there is no inspection goods, because of X-ray is transmitted 100%, transmission rate become 100%. But when there is inspection goods, transmission rate is decreased due to X-ray was absorbed. In case of contaminant was mixed in the inspection goods, the transmission rate that lower than the normal one from the goods is recognized as signal from contaminant.

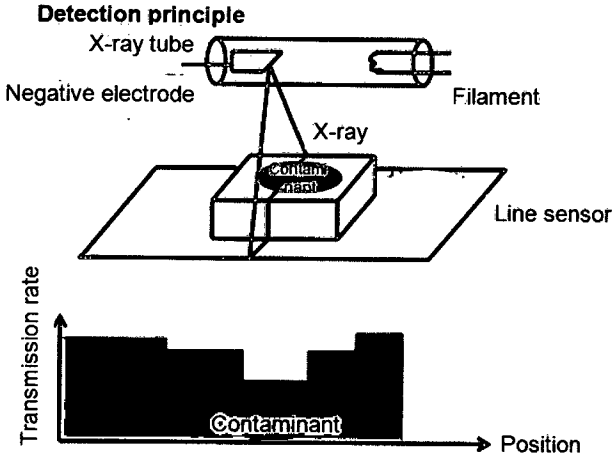

Figure 1.3 Principle of X-ray inspection device

At the present, X-ray inspection device could detect metallic contaminant with size more than 100μm[8]. Also, could detect plastic, bones and other non-metallic contaminant.

However, the disadvantage of X-ray inspection device is difficult to detect things with small specific weight such as hair, rust and etc. Moreover, there is a problem of the viewpoint of safety such as X-ray leakage, and it is important to strictly handle and safety control the device.

1.3.2 High temperature superconductor SQUID detection device

SQUID is derived from Superconducting Quantum Interference Device. The quantized magnetic field is formed in the hole of superconductor ring as magnetic flux. This phenomenon was used by superconducting electron probe known as SQUID that could be used as high sensitivity magnetic sensor.

The detection technology of metallic contaminant using high temperature superconductor SQUID is recently developed[1], and the outline diagram is shown in Figure 1.5. Figure 1.4 shows the shape of high temperature superconductor SQUID sensor used in the device.

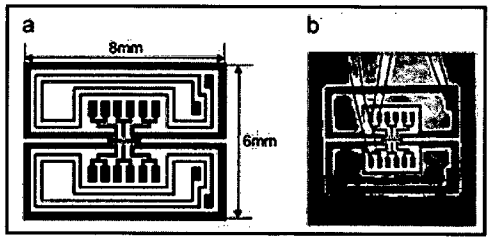

Figure 1.4 High temperature superconductor SQUID sensor

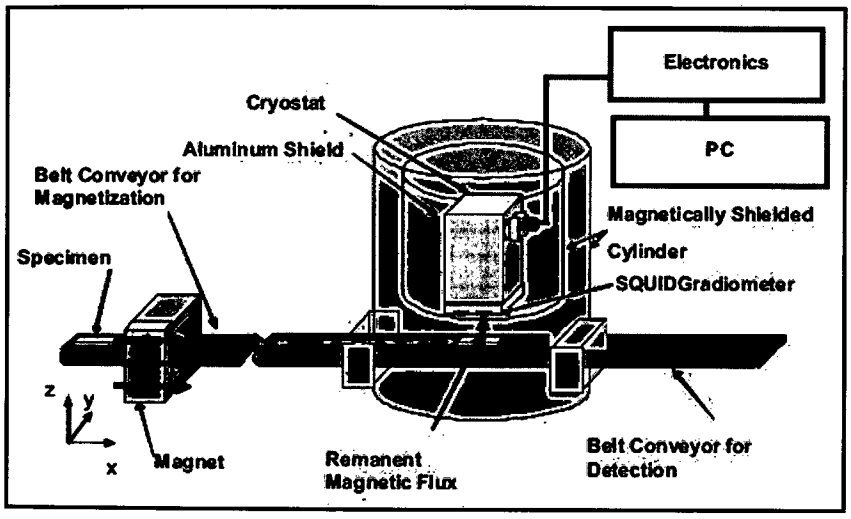

Figure 1.5 Outline diagram of the detection technology of metallic contaminant using high temperature superconductor SQUID.

Using this device, after the sample is magnetized, high temperature superconductor SQUID sensor is measuring the remanent magnetic field of sample and detecting remanent magnetic field of metal piece, this device can be used at production line to detect a very small piece of metallic contaminant. The measurement sensitivity of SQUID is high that about 50μm ferromagnetic metal piece can be detected was reported.

However, a cooling medium or cryogenic refrigerator is necessary for SQUID operation, therefore this would lead to the problem such as total measurement system becomes large size and expensive.

1.4 Hall probe

1.4.1 Introduction

Hall probe that used for the magnetic field measurement is two-dimensionally scanned on sample surface. Thus, two-dimensional magnetic field distribution of sample could be measured. First, Hall probe, which can measure magnetic field, and the composition of magnetic field measurement device that using it are explained in details below. And, the example of previous research that used Hall probe is also described.

1.4.2 Operation principle of Hall probe

Hall probe is a magnetic field sensor that used Hall Effect, or known as Hall Effect magnetic sensor, which can directly change magnetic to electric. Figure 1.6 shows a rectangular section of thin conductor (thickness t, width a) is placed vertically in a uniform magnetic field (magnetic flux density B), and the current I is considered to flow in x direction. Then, the current flew in the conductor is carried by electron that is moved in -x direction. The electron moved with velocity v is resulted to Lorentz force $\boldsymbol{F} = e\boldsymbol{v} \times \boldsymbol{B}$ due to the existence of magnetic flux density, that cause the electron is collected at -y direction of conductor edge and positive charge at y direction of conductor edge. These then generate the electric field $Ey = E_{\mathrm{H}}(< 0)$.

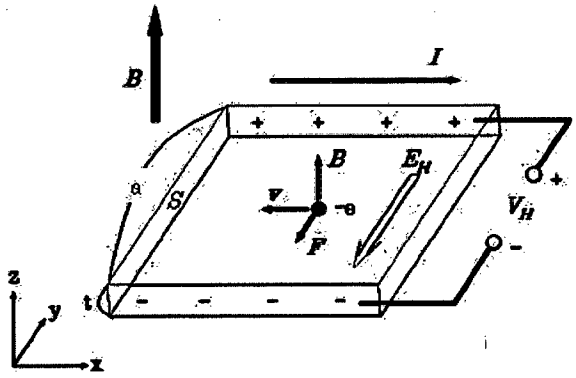

Figure 1.6 Hall Effect

In the stationary state, the point of electron is considered to move only in x direction, not in y direction to find the value of E_{H}. The balance of force by electric field E_{H} and force by magnetic flux density is assumed to become

$$E_{\mathrm{H}} = vB \qquad (1-1)$$

Using the relation between velocity of electron and density of current, $\boldsymbol{i} = -nev$

$$I = iS = -nevS \qquad (1-2)$$

is obtained.

Here, $S = at$ is sectional area of conductor plate. Then, it becomes

$$EH = \frac{IB}{neS} \qquad (1-3)$$

Electric potential, generated by Hall Effect in y direction becomes

$$V_{\mathrm{H}} = -E_{\mathrm{H}}a = \frac{IB}{net} = R_{\mathrm{H}}\frac{IB}{t} > 0 \qquad (1-4)$$

This is known as a Hall voltage. If the current that assumed as charged particles is positive, it become $E_{\mathrm{H}} > 0$ and $V_{\mathrm{H}} < 0$ with sign inversion. Here, B is the external field of magnetic flux and $|R_{\mathrm{H}}| = 1/ne$ can be written where R_{H} is the Hall coefficient, e is electron charge, and n is carrier density. From equation$(1-4)$, to obtain large V_{H}, thin layer of active material, material with small carrier density and large amount of current is necessary.

At the present, material of Hall probe is mainly semiconductor with III-V family compound such as GaAs, InSb, Si and other. Hall coefficient is influenced by electron mobility, thus semiconductor with high mobility tend to be the material as listed above. The structure of Hall probe is formed with 2 output electrodes, and active layer. The active layer is formed by deposition of InSb, injection of ion in GaAs and other appropriate method of each material. As a result, output voltage of Hall probe is actually smaller than that calculated from equation $(1-4)$ as electrode shape is assumed as a point, in constant current operation, V_{H} is

$$V_{\mathrm{H}} = G_{\mathrm{H}}R_{\mathrm{H}}\frac{IB}{t} \qquad (1-5)$$

and in constant voltage operation,

$$V_{\mathrm{H}} = G_{\mathrm{H}}\frac{w}{l}\mu \times V \times B \qquad (1-6)$$

can be expressed where μ is hole mobility, G_{H} is pattern factor, w and l is pattern width and length respectively. For lead frame, non-magnetic material must be used.

1.4.3 Characteristic of Hall probe

The output characteristic of an ideal Hall probe is assured to be shown according to equation $(1-5)$ and $(1-6)$, but is actually depend on the non-uniformity of current distribution during crystallization, atmosphere temperature and the magneto-resistance effect.

(1) Unbalanced voltage

For an ideal Hall probe, when $\boldsymbol{B}=0$, equation $(1-4)$ should become $V_{\mathrm{H}}=0$, but in fact, because of the non-uniformity of current distribution during crystallization and asymmetric main terminal, even without the presence of external magnetic field, the voltage is slightly generated. This is known as unbalanced voltage. Furthermore, it is important to care that the balanced voltage is depending on atmosphere temperature.

(2) Temperature dependence

The output voltage of Hall probe is decreased with the increasing atmosphere temperature. This phenomenon is occurred in both case of constant voltage operation and constant current operation. From equation$(1-6)$, at constant voltage operation, it contributed from hole mobility temperature dependence is known. As well as equation$(1-5)$, temperature dependence of constant current operation is influenced by carrier mobility temperature dependence is also known. Therefore, the temperature dependence of output voltage should be as small as possible, in case either at constant voltage or constant current operation, the material of Hall probe should be selected with magnitude relation to temperature dependence of carrier density and hole mobility.

(3) Magnetic field dependence

Equation $(1-6)$ shows the proportional relation between Hall voltage and external magnetic field. However, in fact, the tendency of saturation is shown due to the external magnetic field. This is called the magneto-resistance effect. The magneto-resistance is the phenomenon where the resistance in Hall probe is increased when its current path become longer due to Hall probe driving current path bended caused by the Lorentz Force due to the existence of external magnetic field. According to this, the voltage applied between input electrodes is becoming small compared to the actual value, and the geometrical factor in equation $(1-6)$ is magnetic field dependence, decreased with increasing external magnetic field. This shows overall is magnetic field dependence. Therefore, to obtain probe with good linearity due to existence of external magnetic field, material that has small magneto-resistance effect and pattern with small geometrical factor have to be chosen.

1.4.4 Precaution for using Hall probe

When using Hall probe for the measurement, it is important to use carefully and correctly according to its characteristic. There is a problem which to consider either constant current or constant voltage operation has to be used. In term of Hall voltage accuracy, constant current operation should be used. The reason is because when constant voltage operation is used, due to magneto-resistance, the Hall probe length value l in equation$(1-6)$ is becoming large and this could be significant effect to the Hall voltage. On the other hand, in case of using constant current operation, as shown in equation$(1-5)$, Hall voltage with no distortion could be obtained because does not influenced by probe length value l.

However, at the operation of constant current, although current is constantly flew through Hall probe, if the resistance of Hall probe is changed by magneto-resistance effect, voltage value that applied to Hall probe could be changed. This can be resulted to the temperature change in unbalanced voltage that leads to its temperature characteristic decreased and therefore need to take attention.

1.4.5 Magnetic field distribution measurement device using Hall probe

Figure 1.7 illustrates the magnetic field distribution measurement device using Hall probe. Hall probe is fixed at the end of Bakelite arm and is attached to x-y stage of device. From this, Hall probe is moved in two-dimension on the surface of sample. Constant current of 10mA was used to drive Hall probe. Measurement result is obtained by reading voltage value of digital voltmeter and calculating magnetic flux density by the calibration with Hall coefficient. In addition, when applying current to the Hall probe for magnetic field distribution measurement, direct current supply is used and its amount can be controlled by PC. The image of Hall probe for measurement is shown in Figure 1.8 and its specifications are shown in Table 1.2. As shown in Figure 1.8, Hall probe is located at the centre (sign of +) of the package, and 0.5mm of distance from package surface. This corresponds to the minimum lift-off distance of Hall probe from the sample. However, in fact, lift-off distance might be increased due to use of tape for setting up the sample. Moreover, magnetic field component that detected by Hall probe is in the normal direction (z) against package plane (and sample plane).

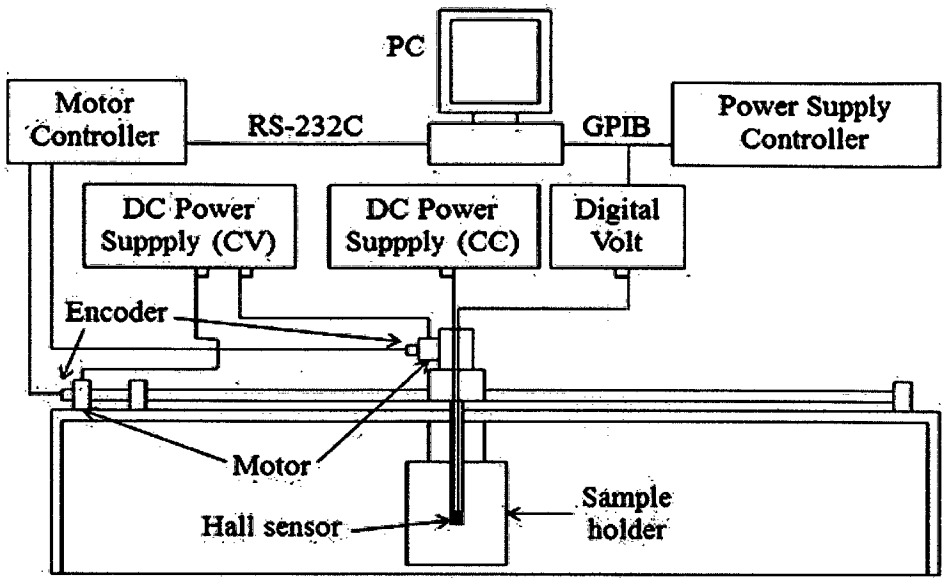

Figure 1.7 Illustration of magnetic field distribution measurement device using Hall probe

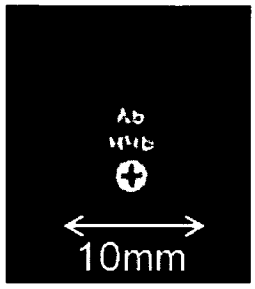

Figure 1.8 Image of Hall probe (view of package plane)

Table 1.2 Specifications of Hall probe

Manufactured by AREPOC	
Model number	HHP-VP
External dimension	7×5×1 [mm]
Sensitivity	78.3 [μV/T]
Lift-off distance	0.5 [mm]
Active area	50×50 [μm]

1.4.6 Previous research by Hall probe and application for metallic contaminant detection

In the research, the magnetic field measurement device using Hall probe, at first, the application of instrumentation technology to find fatigue damage of steel was studied, and micro-crack and fatigue growth on stainless steel (SUS) and low-carbon steel rod could be evaluated has been confirmed. The specific research on the welding point of SUS pipe and the application for quality evaluation technology of Friction Stir Welding (FSW) material on SUS-A1 has been also examined. In addition, the evaluation of uniformity of high temperature superconductor by using this device was successfully done. Also, the non-destructive evaluation of non-uniformity of electrical characteristic in the direction of wire section width and longitudinal direction of Ag-sheathed high temperature superconducting wire that has been introduced with high resistivity barrier and twisted superconductor filament in order to reduce Ac losses had been carried out successfully using the device[10][11].

On the other hand, magnetic field detection sensitivity is the most important in order to use magnetic sensor for detection of metallic contaminant mixed in battery parts. The detection sensitivity of Hall probe is shown in Figure 1.9, and its fundamental weak point is low in several digits compared with SQUID. However, if metallic contaminant is limited to iron and other ferromagnetic metal, and by applying external magnetic field, the magnetized contaminant will increase generating magnetic field that can be detected. Thus, the weak point can be countered and there is a possibility to the application of metallic contaminant detection technology is suggested.

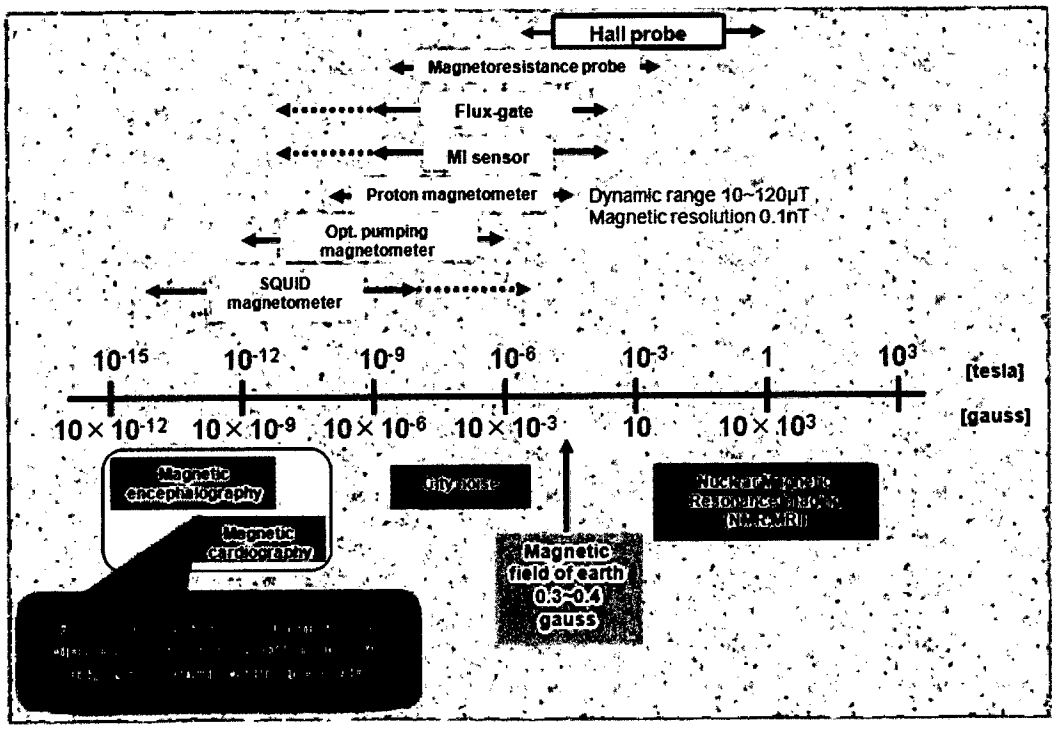

Figure 1.9 Types of magnetic sensor and detection sensitivity

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CHAPTER 2

Experimental Procedure

2.1 Introduction

First of all, we explain the method for the preparation of the electrode of lithium ion battery in this chapter. In our research, lithium cobalt oxide, LiCoO2 (Nippon Chemistry Industrial Co., Ltd.) was used as cathode material to prepare the electrode coating[1]. After that, measurement sample was made by adding a piece of metallic contaminant in the prepared electrode. The preparation of measurement sample, the method of measurement, the method of analysis and evaluation were explained here. Iron wire and iron particle were used for metallic contaminant in our research as well.

2.2 Electrode for lithium-ion battery preparation procedure

2.2.1 Materials for electrode preparation

In our research, lithium cobalt oxide ($LiCoO_2$), now widely used as positive electrode or cathode for lithium ion battery, was used to prepare the electrode. Also, acetylene black (AB) was used as conducting material. The specifications of $LiCoO_2$ and AB as materials for the preparation of the electrode are showed in table 2.1 and 2.2. Moreover, PolyVinylidene diFluoride (PVdF) was used as the electrode binder material for cathode and N-methyl-2-pyrrolidone (NMP) was used as a solvent, and the specifications of both materials are showed in table 2.3 and 2.4 respectively.

Table 2.1 The specifications of $LiCoO_2$

Name or Label	C-10
Manufacturer	Nippon Chemical Industrial Co., Ltd.
Average particles size (μm)	10.5
Specific surface area (m^2/g)	0.21

Table 2.2 The specifications of AB

Name or Label	Acetylene Black
Manufacturer	Nippon Chemical Industrial Co., Ltd.
	50 % press

Table 2.3 The specifications of PVdF

	Binder material for cathode
Name or Label	L#7208
Manufacturer	Kureha Corporation
The resin content (%)	8
Weight average molecular weight	About 630 thousand
Thickness (mPa·s)	2350
Moisture (%)	≦ 0.1

Table 2.4 The specifications of NMP

Name or Label	N-methyl-2-pyrrolidone
Manufacturer	Kishida Chemical Co., Ltd.
Purity (%)	99.5
Chemical formula	$CH_3NC_4H_6O$

2.2.2 Electrode preparation

2.2.2.1 Material weight calculation method for $LiCoO_2$ electrode preparation

$LiCoO_2$ cathode was made by based on the weight ratio, $LiCoO_2$: AB : PVdF : NMP = 90 : 6 : 4 : 90, that the cathode slurry was made and coated on aluminum foil. The material weight calculation is showed as below.

1. Weight of $LiCoO_2$

   $LiCoO_2$ was assumed to be 7 g.

2. Weight of AB

   Weight of AB is written as M_{AB}g and calculated as shown below

$$90:7 = 6:M_{AB}$$

$$M_{AB} = \frac{6\times7}{90} = \frac{42}{90} \approx 0.4667 \text{ g}$$

3. Weight of PVdF

Necessary Weight of PVdF solid component in the binder solution is written as M_{PVdF}g, and calculated same like AB.

$$90:7 = 4:M_{PVdF}$$

$$M_{PVdF} = \frac{7\times4}{90} = \frac{28}{90} \approx 0.3112\ g$$

Solid component of PVdF solution is 8wt.%, therefore necessary weight of PVdF solution is written as $M_{PVdF\_sol'n}$ g and become

$$1:0.08 = M_{PVdF\_sol'n}:0.3112\ g$$

$$M_{PVdF\_sol'n} = \frac{0.3112}{0.08} = 3.89\ g$$

4. Weight of NMP

Weight of NMP in PVdF solution as a solvent is

$$3.89\ g - 0.3112\ g = 3.5788\ g$$

Weight of NMP needed is written as M_{NMP}g and calculated as shown below.

$$90:7 = 90:M_{NMP}$$

$$M_{NMP} = \frac{90\times7}{90} = 7\ g$$

Thus, necessary weight of NMP to be used is

$$7\ g - 3.5788\ g = 3.4212\ g$$

2.2.2.2 $LiCoO_2$ electrode preparation process

$LiCoO_2$ electrode preparation process is showed in Figure 2.1. The details of the procedure are described in the following 1-10.

1. $LiCoO_2$ and AB were used and weighed respectively based on the weight ratio, $LiCoO_2$:AB=90:6, that was calculated by electron balance, and was put in pot 2 (Kinki Container、BHR-150、150cc). The total weight of the sample in pot 2, pot 2 and mixer adaptor were weighed and the sample was mixed using the planetary mixer at 2000 rpm in 5 min.

2. PVdF and NMP solution were used and weighed respectively based on the weight ratio, PVdF:NMP =4:90, that calculated by electron balance, and was put in pot 1. The total weight of the sample in pot 1, pot 1 and mixer adaptor were weighed and the sample were mixed using the mixer at 1000rpm in 1 min.